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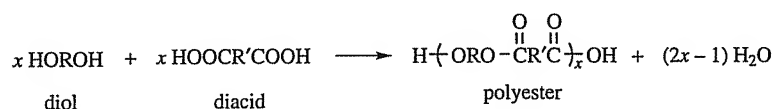
POLYMERS

1. Introduction

Polymers are very large molecules made by covalently binding many smaller molecules. The word polymer is derived from the Greek *poly* (many) and *meros* (part). The size of polymer molecules imparts many interesting and useful properties not shared by low molecular weight materials. Polymers are the fundamental materials of plastics, rubbers and most fibers, and surface coatings and

adhesives, and as such are essential to modern society. Also, many important constituents of living organisms, eg, proteins (qv) and cellulose (qv), are biopolymers (qv).

2. Classification and Nomenclature

Polymers were initially classified according to their response to temperature. Those that are softened (plasticized) reversibly by heat are known as thermoplastics. By analogy, wax behaves as a thermoplastic. Others, though they might initially be liquid or soften once upon heating, undergo a curing (setting) reaction that solidifies them, and further heating leads only to degradation. These are known as thermosets. Again by analogy, an egg behaves as a thermoset. The ability of polymers to soften and flow at least once is one of their most valuable assets, as it allows them to be formed into complex shapes easily and inexpensively.
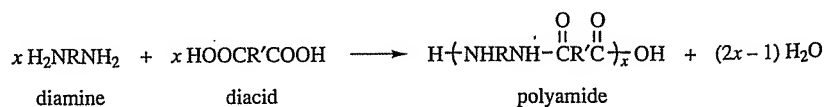
In general, polymers are formed by two types of reactions: condensation and addition. The formation of a polyester by polycondensation may be illustrated as follows.

$$x \text{ HOROH} \; + \; x \text{ HOOCR'COOH} \; \longrightarrow \; \text{H} \left(\text{ORO} - \overset{\overset{\text{O}}{\|}}{\text{C}} \text{R'} \overset{\overset{\text{O}}{\|}}{\text{C}} \right)_x \text{OH} \; + \; (2x-1) \, \text{H}_2\text{O}$$

$$\quad\;\; \text{diol} \qquad\qquad \text{diacid} \qquad\qquad\qquad\qquad\qquad \text{polyester}$$

In the polyester formula shown, parentheses enclose the repeating unit. The quantity x is the degree of polymerization, sometimes also called the chain length, the number of repeating units strung together like identical beads on a string. Neglecting the ends of the molecule, which is usually justified for large x, the molecular weight M of the polymer molecule is given by $M = mx$, where m is the molecular weight of the repeating unit. Since x can easily be in the thousands, it is not surprising that the term macromolecules is also used to describe these materials.

The ester linkage in the repeating unit characterizes polyesters. R and R' represent portions of the monomer molecule that do not participate in the polymerization. They may vary widely, giving rise to many different polyesters. Poly(ethylene terephthalate) (PET), made from ethylene glycol ($\text{R} = (\text{CH}_2)_2$) and terephthalic acid ($\text{R}' = -\bigcirc-$), is familiar in the form of soda bottles, recording tape, and polyester fiber (see FIBERS, POLYESTER).

Another common polycondensation involves reaction of diamines and diacids to form polyamides, commonly called nylons:

$$x \text{ H}_2\text{NRNH}_2 \; + \; x \text{ HOOCR'COOH} \; \longrightarrow \; \text{H} \left(\text{NHRNH} - \overset{\overset{\text{O}}{\|}}{\text{C}} \text{R'} \overset{\overset{\text{O}}{\|}}{\text{C}} \right)_x \text{OH} \; + \; (2x-1) \, \text{H}_2\text{O}$$

$$\quad\;\; \text{diamine} \qquad\qquad \text{diacid} \qquad\qquad\qquad\qquad \text{polyamide}$$

The amide linkage characterizes nylons. In the first commercial nylon, nylon-6,6, $\text{R} = (\text{CH}_2)_6$ and $\text{R}' = (\text{CH}_2)_4$. Nylon-6,6 is familiar as a textile fiber (nylon stockings) and a molded plastic (see POLYAMIDES).

The two complementary functional groups that react to form condensation polymers may also occur in a single monomer, eg, a hydroxy acid, HO–R–COOH, or an amino acid, H_2N–R–COOH. In some cases, such monomers self-condense to a cyclic structure, which is what actually polymerizes. For example, ϵ-caprolactam (**1**) can be thought of as the self-condensation product of an amino acid. Caprolactam undergoes a ring-opening polymerization to form another

$$H_2N\text{-}(CH_2)_5\text{-}COOH \longrightarrow$$

(**1**)
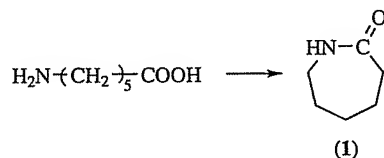
important nylon, nylon-6 (see CAPROLACTAM). Even though no water is eliminated in the actual polymerization step, the polymer is usually considered a condensation polymer. Table 1 illustrates some other important condensation polymers.

$$x\,(\mathbf{1}) \longrightarrow \ \ \ \left(NH(CH_2)_5\overset{\overset{\displaystyle O}{\|}}{C}\right)_{\!\!x}$$
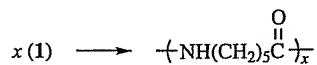
Addition or chain-growth polymerization involves the opening of a double bond to form new bonds with adjacent monomers, as typified by the polymerization of ethylene to polyethylene:
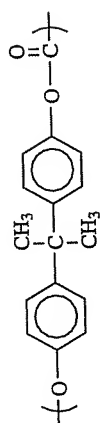
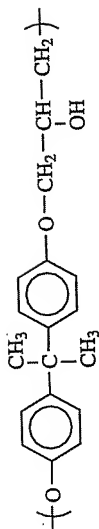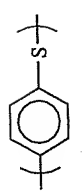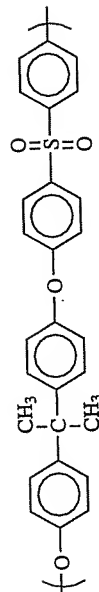$$x\,H_2C{=}CH_2 \longrightarrow (CH_2{-}CH_2)_x$$
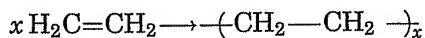
Because no molecule is split out, the molecular weight of the repeating unit is identical to that of the monomer. Vinyl monomers, $H_2C{=}CHR$ (Table 2) undergo addition polymerization to form many important and familiar polymers. Diene (two double bonds) monomers also undergo addition polymerization. Normally, one double bond remains, leaving an unsaturated polymer, with one double bond per repeating unit. These double bonds provide sites for subsequent reaction, eg, vulcanization.
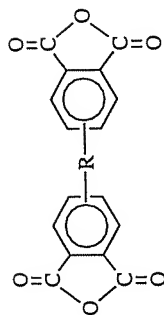
In terms of molecular structure, there are three principal categories of polymers, illustrated schematically in Figure 1. If each monomer is difunctional, that is, can react with other monomers at two points, a linear polymer is formed. All the examples given above are linear polymers. Polymers that contain two different repeating units, say A and B, are known as copolymers (qv). A linear polymer with a random (AABBABAAABABB) arrangement of the repeating units is a random or statistical copolymer, or just copolymer. It is termed poly(A–*co*–B), with the primary constituent listed first. A molecule in which the two repeating units are arranged in long, contiguous blocks ($[A]_{\overline{x}}$——$[B]_y$) is a block (*b*) copolymer, poly(A–*b*–B).

A few points of tri- or higher functionality introduced along the polymer chains, either intentionally or through side reactions, give a branched polymer. A branched structure with the backbone consisting of one repeating unit (A) and the branches of another (B), is a graft (*g*) copolymer, poly(A–*g*–B). Dendrimers are a more recent development. They are molecules that branch repeatedly as they grow outward from a central core (1–3).
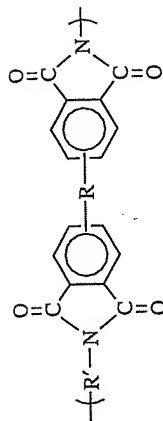
Table 1. Some Commercial Condensation Polymers

Polymer	Monomers	Repeating unit	Eliminated molecule[a]
polycarbonate	bisphenol A[b] $HO-C_6H_4-C(CH_3)_2-C_6H_4-OH$	$-[O-C_6H_4-C(CH_3)_2-C_6H_4-O-\overset{O}{\overset{\|}{C}}-]-$	HCl
epoxy resin	epichlorohydrin[c] $H_2C\overset{O}{-}CH-CH_2-Cl$	$-[O-C_6H_4-C(CH_3)_2-C_6H_4-O-CH_2-\underset{OH}{CH}-CH_2]-$	HCl
polydimethylsiloxane (silicone rubber)	dimethyl dichlorosilane[d] $Cl-\underset{CH_3}{\overset{CH_3}{Si}}-Cl$	$-[\underset{CH_3}{\overset{CH_3}{Si}}-O]-$	HCl
poly(phenylene sulfide)	$Cl-C_6H_4-Cl \ + \ Na_2S$	$-[C_6H_4-S]-$	NaCl
polysulfone[e]	$Cl-C_6H_4-\overset{O}{\underset{O}{\overset{\|}{S}}}-C_6H_4-Cl^{f}$	$-[O-C_6H_4-C(CH_3)_2-C_6H_4-O-C_6H_4-\overset{O}{\underset{O}{\overset{\|}{S}}}-C_6H_4]-$	NaCl

polyimide

dianhydride[g]

$+ H_2O$

[a] A true condensation reaction is characterized by elimination of a small molecule when the monomers condense to form the repeating unit.
[b] Reacts with phosgene $COCl_2$ to form the repeat unit shown (see POLYCARBONATES).
[c] Reacts with bisphenol A to form the repeat units shown (see EPOXY RESINS).
[d] Reacts with H_2O to form the repeat units shown (see SILICON COMPOUNDS, SILICONES).
[e] See Polymers containing sulfur.
[f] Reacts with the disodium salt of bisphenol A.
[g] Reacts with diamine $H_2N-R'-NH_2$ (see POLYIMIDES).

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Table 2. **Some Vinyl Monomers, CH$_2$=CHR**

R	Common name	Polymer repeating unit	*Encyclopedia* reference
Cl	vinyl chloride	$+CH_2-CHCl+$	VINYL POLYMERS, VINYL CHLORIDE POLYMERS
C$_6$H$_5$	styrene	$+CH_2-CH(C_6H_5)+$	STYRENE PLASTICS
CH$_3$	propylene	$+CH_2-CH(CH_3)+$	OLEFIN POLYMERS, POLYPROPYLENE
C≡N	acrylonitrile	$+CH_2-CH_2CN+$	ACRYLONITRILE POLYMERS
COOH	acrylic acid	$+CH_2-CH+$ COOH	ACRYLIC ACID AND DERIVATIVES
OOCCH$_3$	vinyl acetate	$+CH_2-CH+$ CH$_3$COO	VINYL POLYMERS, VINYL ACETATE POLYMERS
CONH$_2$	acrylamide	$+CH_2-CH+$ O=C-NH$_2$	ACRYLAMIDE POLYMERS

As the length and frequency of branches increase, they may ultimately reach from chain to chain. If all the chains are connected together, a cross-linked or network polymer is formed. Cross-links may be built in during the polymerization reaction by incorporation of sufficient tri- or higher functional monomers, or
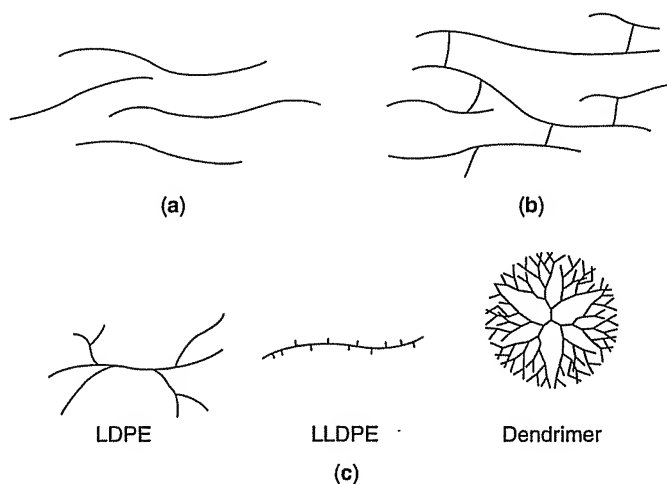

Fig. 1. Schematic diagram of polymer structures: (a) linear; (b) cross-linked; and (c) branched, where LDPE = low density polyethylene and LLDPE = linear low density polyethylene.

may be created chemically or by radiation between previously formed linear or branched molecules (curing or vulcanization). For example, a liquid epoxy (Table 1) oligomer (low molecular weight polymer) with $x \approx 6-8$ is cured to a cross-linked solid by reaction of the hydroxyl and terminal epoxide groups with a diamine or acid anydride. In a fully cross-linked polymer, all the atoms are connected to one another by covalent bonds, so the entire macroscopic polymer mass is literally a single molecule. Thus, the cross-linked polyester in a bowling ball has a molecular weight on the order of 10^{27} g/mol.

3. Structure and Properties

Various levels of structure ultimately determine the properties of a polymer. The characterization of structure and how it influences properties is outlined in the following.

3.1. Molecular Weights.
With the exception of some naturally occurring polymers, all linear and branched polymers consist of molecules with a distribution of molecular weights. Two average molecular weights are commonly defined; the number-average, $\overline{M}_n$, and the weight-average, $\overline{M}_w$:

$$\overline{M}_n = \frac{W}{N} = \frac{\sum_{x=1}^{\infty} n_x M_x}{\sum_{x=1}^{\infty} n_x}$$

$$\overline{M}_w = \frac{\sum w_x M_x}{\sum w_x} = \frac{\sum n_x M_x^2}{\sum n_x M_x}$$

where W = total sample weight = $\sum_{x=1}^{\infty} w_x = \sum_{x=1}^{\infty} n_x M_x$; w_x = total weight of x-mer; N = total number of moles in the sample (of all sizes) = $\sum_{x=1}^{\infty} n_x$; n_x = number of moles of x-mer; M_x = molecular weight of x-mer.

It may be shown that $\overline{M}_w \geq \overline{M}_n$. The two are equal only for a monodisperse material, in which all molecules are the same size. The ratio $\overline{M}_w / \overline{M}_n$ is known as the polydispersity index and is a measure of the breadth of the molecular weight distribution. Values range from about 1.02 for carefully fractionated samples or certain polymers produced by anionic polymerization, to 20 or more for some commercial polyethylenes.

Colligative property techniques that measure the moles of polymer in solution give $\overline{M}_n$. These include membrane and vapor-pressure osmometry and freezing-point depression. Procedures which, in effect, determine the mass of polymer at each size level give $\overline{M}_w$. These include light scattering and sedimentation in an ultracentrifuge. Another technique, intrinsic viscosity, makes use of the large increase in viscosity caused by relatively small amounts of polymeric solute. Intrinsic viscosity gives yet another average molecular weight, $\overline{M}_v$ (viscosity-average), which is between $\overline{M}_n$ and M_w, but is closer to the latter. Unlike the other techniques mentioned, it must be calibrated with monodisperse samples of known molecular weight. Still, because much calibration data are available in the literature (4), the necessary equipment is inexpensive, and the measurements are precise, straightforward, and rapid, it is used frequently.